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Hans-Erik Hjelmroth et al.

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For: INK COMPOSITION FOR INK-JETTING UPON SUBSTRATES FOR A PRINT FORM, PROCESS FOR PRODUCING IT, AND METHOD OF PREPARING A LITHOGRAPHIC PRINT FORM

Examiner: Not Yet Assigned

AFFIRMATION OF PRIORITY CLAIM

Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450

Dear Sir:

Applicant hereby claims priority under 35 U.S.C. 119 based on the following prior foreign application filed in the following foreign country on the date indicated:

Country	Application No.	Date
Denmark	PA200201633	October 28, 2002

A certified copy of the aforesaid Patent Application was received by the International Bureau on November 3, 2003 during the pendency of International Application No. PCT/DK03/00724. A copy of Form PCT/IB/304 is enclosed.

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Respectfully submitted,

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Title: Ink composition for ink-jetting upon substrates for a print form, process for producing it, and method of preparing a lithographic print form

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This is to certify that the attached documents are exact copies of the above mentioned patent application as originally filed.

Patent- og Varemærkestyrelsen
Økonomi- og Erhvervsministeriet

28 October 2003

Pia Høybye-Olsen

PATENT- OG VAREMÆRKESTYRELSEN

PRIORITY DOCUMENT
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28 OKT. 2002

PVS

Ink composition for ink-jetting upon substrates for a print form, process for producing it, and method of preparing a lithographic print form

FIELD OF THE INVENTION

This invention relates to an ink for use in the preparation of printing plates. More particularly it relates to a composition comprising a polymeric compound which is suitable for ink-jetting on a substrate, which is usually a metal plate but not limited thereto, which, after treatment, can be used as a printing form in lithographic printing.

BACKGROUND OF INVENTION

In the offset lithographic printing method a developed planographic printing plate having oleophilic image areas and hydrophilic non-image areas has long been used. When water is applied to such a plate, the water will form a film on the hydrophilic areas, which are the non-image areas of the plate, but the water will contact into tiny droplets on the oleophilic plate areas. When an oil-based ink composition is applied to the plate, it will not ink the water film of the non-image, but it will emulsify the water droplets on the water repellant image areas, which then take up ink. The resulting image is transferred, or "offset", onto a rubber blanket which is then used to print onto a medium such as paper.

The plates used to prepare the printing plate may be, but are not limited to, aluminium plates with different surface treatments. These surfaces can be anodized, grained or silicated in order to obtain a surface having e.g. acidic, amphoteric or alkaline properties.

After this surface treatment ink, resin, wax, etc. are used to create the oleophilic areas of the printing plate. The printing plate is then dried, cured, heated, washed or subjected to other treatment to prepare the final plate.

It is known to print on these plates with different kind of inks using ink-jetting techniques e.g. piezo, thermal, bubble jet, drop on demand or continuous ink jet. For this purpose, the ink must possess certain characteristics. It must have a surface tension within certain limits. If the surface tension of the ink is lower than the surface tension of the metal, the ink will spread. If the surface energy is

too high, the contact angle, which is given by Young's Equation, will be more than 90°, which will cause the drop to bounce off.

US 2002/0109763 A1 discloses the use of boron acids and boron esters as the component of the ink that binds to the surface of the plate. These inks are suitable for oxidized metallic surfaces and particularly anodised aluminium surfaces.

EP 1 157 825 A1 discloses the use of phospoesters as the component that makes the printing plate oleophilic. These inks are also limited to use on an oxidized metallic surface which has preferably been anodised.

EP 1 157 827 A1 discloses the use of heterocyclic compounds as the oleophilizing agent in the ink. These inks are also mainly limited to use on an oxidized metallic surface which has preferably been anodised.

WO0046038 discloses the use of certain polymers and copolymers as the oleophilizing component in an ink composition. It discloses the use of partly or fully neutralized acidic polymers for use on alkaline plates. It further discloses the use of partly or fully neutralized alkaline polymers containing a plurality of tertiary amine groups as a part of the polymer backbone for use on acidic plates.

The previously mentioned inks all have the setback that they are only suitable for certain plates, e.g. acid polymers for alkaline plates and alkaline polymers for acidic plates. It would be a big advantage if one ink could be used on any kind of printing plate.

Furthermore the previous inks have a relatively long drying time. An ink which dries and hardens fast will facilitate the handling of printing plates because they will be less sensitive to shock.

SUMMARY OF THE INVENTION

An object of the present invention is to provide a fluid composition which may be used as an ink for ink jetting on all types of plates to produce a printable media. Furthermore it is an object of the invention to provide an ink which dries and hardens fast after it has been applied to the printing plate.

The invention is based on the discovery that amidized acidic polymers and copolymers can bind to all types of plates and that they dry very fast and form integrated structures faster after being sprayed on the plate and subjected to heating. An even better ink is obtained if the amidized acidic polymer is mixed with fatty acids and optionally one or more transition metals By adding fatty acids and metal ions to the ink composition containing amidized acidic polymers a particularly suitable ink is obtained.

This invention provides an ink comprising a polymer or copolymer with an acidic group, where said group is converted to the corresponding amide. This ink is suitable for ink-jetting. Optionally the polymer of the ink can be modified with fatty acids and one or more metals/metal complexes chosen from the group of transition metals.

This invention also provides a process for producing such inks comprising the steps:

a) treating an acid containing polymer or copolymer with an amine,
b) adjusting pH to above 7,
c) optionally adding fatty acid, oil or wax,
d) optionally adding one or more transition metals,
e) optionally adding colour.

This invention further provides a method of preparing a lithographic print form which comprises the steps:

a) treating a substrate with an ink according to the invention,
b) drying the substrate,
c) heating the substrate.

The ink of the invention is suitable for ink jetting in all its forms, e.g. bubble jet, piezo, thermal, drop on demand or continuous ink jet.

The advantage of this invention is that the ink of the invention can be used on almost any metal plate, and at least on any aluminium surface. The ink dries fast and has less tendency to generate bubbles in the ink and is therefore particularly suitable in the printing industry.

In one embodiment the ink is water soluble which is desirable due to the resulting cleaner printing methods.

DETAILED DESCRIPTION OF THE INVENTION

The applicant has discovered that an ink composition comprising a polymer with an acid group which has been converted to the corresponding amide can bind hard enough to both acidic and alkaline metal surfaces to be useful in producing lithografic printing forms. The ink is suitable for ink-jetting, e.g. bubble jet, piezo, thermal, drop on demand or continuous ink jet. The ink may be further improved by treating it with fatty acids and optionally one or more metals from the group of transition metals.

The Ink

The ink according to the invention comprises a polymer or a copolymer with an acid group. The monomers with the acidic group may be chosen from, but are not limited to, acrylic acid, methacrylic acid, maleic acid, maleic acid anhydride, fumaric acid, fumaric acid anhydride. Further monomers used in the copolymers include, but are not limited to, styrene, sulfonated styrene, vinyl, etc. The polymers may be, but are not limited to, block, graft, random-block or random-graft polymers

Particularly suited polymers are Joncryl polymers which are styrene-acrylate polymers. Especially polymers with an average molar mass above 10 000 g/mole, and optimally above 14 000 g/mole, may be used, one such polymer being Joncryl 690.

As mentioned, the ink may optionally comprise a fatty acid, a wax or any kind of analog material which binds to the amide. When used, the fatty acid or fatty acid alcohol is present from 0.001 % by weight to saturation. The fatty acid may optionally be based on a saponified polymer. The fatty acid may be any fatty acid containing 4 to 26 carbon atoms. The fatty acid may be saturated or unsaturated. It may contain one or more additional functional groups besides the acid group. These functional groups may be, but are not limited to, such chosen from the list: amines, imines, esters, ethers, ketones, aldehydes, sulfates, sulfones, sulfides, phosphates and phosphoesters. The fatty acids may be, but are not

limited to: lauric, myristic, palmitic, stearic, arachidic, palmitoleic, oleic, linoleic, and linolenic acids. A particularly suited fatty acid is lanolin, and the lanolinate-alcohols are equally suited.

The ink may also comprise any form of organic or non organic oil that binds to the amidized polymer either at the amide bond or at another site of the polymer. Said oils may be chosen from, but are not limited to, silicone oils or ether oils.

In a preferred embodiment the ink also comprises one or more transition metals. When used, the transition metal/metals is/are present in concentrations from 0.001 to 10 % by weight.

The ink may further contain from 5 to 90% water.

In another embodiment the starting material, i.e. the polymer or copolymer, may be bought as an amide. The polymer or copolymer is then treated with base to keep the solution alkaline. One or more of the previously mentioned additives is then applied to the mixture as described for the acidic polymer or copolymer.

The ink may be an emulsion or a solution comprising one or more liquids. In a preferred embodiment one of the liquids is water.

After the amidization a base is added to the mixture in order to keep the mixture alkaline, i.e. pH above 7, also in the case where acidic compounds are added to the mixture. Preferably the pH is kept in the range between 7.5 and 8.5. The added base may be any kind of base, but ammonia is preferred, and especially a 30% aqueous solution of ammonia is preferred.

The resulting ink should have a dynamic viscosity between 1.0 and 5 mPa·s, preferably between 1.5 and 4.5 mPa·s, and optimally between 2.5 and 4.5 mPa·s. It should also have a surface tension between 0.02 and 0.06 N/m and preferably between 0.03 and 0.05 N/m. The surface tension and the dynamic viscosity are adjusted to accurate values within said limits by adding liquids with different surface tensions or by adding surfactants. Said liquids may be, but are not limited to, one or more liquids from the list:

Ethylene glycol monomethyl ether, ethylene glycol dimethyl ether, ethylene glycol monoethyl ether, ethylene glycol diethyl ether, ethylene glycol mono-n-

propyl ether, ethylene glycol monoisopropyl ether, ethylene glycol mono-n-butyl ether, ethylene glycol mono-sec-butyl ether, ethylene glycol monoisobutyl ether, ethylene glycol mono-tert-butyl ether, ethylene glycol mono-n-amyl ether, ethylene glycol mono-n-hexyl ether, propylene glycol monomethyl ether, propylene glycol dimethyl ether, propylene glycol monoethyl ether, propylene glycol diethyl ether, propylene glycol mono-n-propyl ether, propylene glycol monoisopropyl ether, propylene glycol mono-n-butyl ether, propylene glycol mono-sec-butyl ether, propylene glycol monoisobutyl ether, propylene glycol mono-tert-butyl ether, diethylene glycol monomethyl ether, diethylene glycol dimethyl ether, diethylene glycol monoethyl ether, diethylene glycol diethyl ether, diethylene glycol mono-n-propyl ether, diethylene glycol mono-iso-propyl ether, diethylene glycol mono-n-butyl ether, diethylene glycol mono-sec-butyl ether, diethylene glycol monoisobutyl ether, diethylene glycol mono-tert-butyl ether, dipropylene glycol monomethyl ether, dipropylene glycol monoethyl ether, dipropylene glycol mono-n-propyl ether, dipropylene glycol mono-n-butyl ether, polyethylene glycol monopropyl ether, polyethylene glycol monobutyl ether, ethylene glycol, propylene glycol, any alcohol with 1 to 6 carbon atoms e.g methanol, ethanol, n-propanol, 2-propanol etc. It is known from the literature that these compounds will change the surface tension and the viscosity of an aqueous solution. The liquids may be present in amounts from 0.1 to 80 % by weight.

The surfactants may be, but are not limited to, quaternary ammonium salts, ammonium salts, sulfonates, and sulfonic acids. They may be present in amounts from 0.1 to 20 % by weight

The ink in all of its embodiments forms spots after drying and heating to more than 120 °C, preferably heated to between 170 °C and 220 °C, and optimally heated to between 190 °C and 210 °C. These spots form an oleophilic, and preferably hydrophobic, structure which adheres to the substrate of the print form. The dried and hardened ink becomes the printing ink receptive layer of the resulting print form. The ink is oleophilic, and therefore the printing ink adheres to the areas where the ink is deposited on the metal surface (the image areas) On the non-image areas the surface remains hydrophilic, and only water will adhere to those regions. In this application "image" is the term used for both letters and pictures of the lithographic print form. It is on the image that the printing ink is adsorbed.

The ink preferably has a wetting angle between 15° and 65°.

In a preferred embodiment the ink also contains between 0.1 and 20 % by weight of a colour, and optimally the colour is a dye soluble in the mixture. Suitable colours are chromodyes.

The resulting print form should be able to carry out many runs, preferably it should be able to achieve run lengths of more than 50 000 copies, optimally more than 100 000 copies.

PROCESS FOR PRODUCING THE INK

The ink is produced by taking a polymer or copolymer prepared from the previously mentioned monomers, preferably of the type N-p-styrene-N-p-acryl and most preferably a Joncryl 690, and mixing it with an aqueous solution of NH_3. The mixture is heated to between 65 °C and 140 °C, preferably between 70 °C and 100 °C, and optimally about 80 °C. Optionally, a fatty acids, a wax and/or an oil of the previously mentioned kind is added together with a strong base. The mixture is kept heated and the method may optionally take place under pressure, from 0.1 to 150 atm. One or more metals from the group of transition metals may further be added to the mixture.

This base-mixture is diluted with an equal amount of water. Further, 0.1 to 5% of an aqueous NH_3 solution is added, preferably a 30% solution, and optionally a colour. Enough ammonia is added to keep the solution alkaline, even if the colour is acidic, i.e. the solution is kept at a pH >7, and preferably a pH between 7.5 and 8.5.

In an alternative procedure soaps or polysoaps of fatty acids and/or oils and/or soap-analogs are added directly to the method between the polymer and ammonia. These soaps join with the acyl part of the amide or with other functional groups of the polymer. Hereby micelle-like polymer-amide-soap-complexes are formed which are partly soluble in water. After being placed on a substrate and being dried and baked at temperatures above 120 °C, preferably between 170 °C and 220 °C, and optimally between 190 °C and 210 °C, the resulting mixture creates an interlinking cross-binded network. This network binds strongly to the

surface of the substrate, and the resulting product is the lithographic print form. During the heating the ink is burned into the surface of the substrate.

Suitable ink compositions are given in the table below:

Ink no.	1	2	3	4	5	6	7
Sudan IV	1.3	1.3			1.5		
Chromodye Ethyl Red				4.3		4.3	
Chromodye Rodamine B			25				25
Ethanol	10	8	25	23	10	23	25
Dest. water	57.9	47.5	16	62.9	57.9	62.9	15.9
Dowanol	14	12	25		14		25
Ammonia	2	1.6	2	3.3	2	3.3	2
"Joncryl® 690"	14.7	12	7	6.4	14.5	6.4	7
Lanoline		15.2	5				
NaOH		2.4					
Neutral lanoline soap	0.1			0.1	0.1	0.1	0.1

The amounts are % by weight. The base used may be replaced by any base and the soap may be replaced by any soap. Neutral soaps are preferred.

PROCESS OF PREPARING THE PRINTING FORM

An ink according to the invention is applied to the substrate by any kind of ink-jetting. The substrate is then dried and baked at temperatures above 120 °C, preferably between 170 °C and 220 °C, and optimally between 190 °C and 210 °C. The dried ink is the printing image of the print form.

EXAMPLE 1

The amidized Joncryl 690 is prepared by mixing 25 g water-free crystalline random poly-styrene-acryl from Johnson Polymers Inc. in 50 g H_2O with 9 g 30% ammonia with stirring at 80 °C for approximately 30 min. Subsequently, the mixture is diluted with the same amount of water and at least enough ammonia to keep the mixture alkaline (pH>7) even with addition of acidic components.

EXAMPLE 2

An ink as described in Example 1, where 14 g dowanol is mixed with the polymer and the ammonium before the stirring

EXAMPLE 3

To the amidized Joncryl from example 1 lanoline is added to saturation. Hereby complexes of styrene-acryl-amide-fatty acid are created. These complexes are only partly soluble in water and they form small micelles. This mixture is then sprayed on the plate, whereafter the plate is dried and baked at temperatures above 150 °C. During the heating the mixture forms a cross-linking network which binds to aluminium plates. The binding is strong enough to use the aluminium plate as a print form for lithographic printing.

EXAMPLE 4

To the mixture of example 2 chromium (III) complexes are added in an amount of up to 5 % by weight of chromium. This mixture is sprayed on an aluminium plate which is dried and baked as mentioned previously. The network of metal-styrene-acryl-amide-fatty acid now binds even stronger to the aluminium plate. The resulting print form therefore can be used to extended run lengths, more than 100 000 copies.

EXAMPLE 5

A preferred ink composition is 100 g of the amidized Joncryl 690 mixed with 20 g EtOH and 2 g Sudan IV.

EXAMPLE 6

Inks from permanent penol markers 777 and 750 have been painted on aluminium surfaces. Said inks comprise acrylates, Fe-, Zi-, Va-, Mn-, Mb-, Co-, Cr- and Ti-complexes. The complexes of acrylate and the metals bind particularly hard to the aluminium surface, and the alkyl part of the acrylates then provides the oleophilic and hydrophobic areas necessary for use in producing a print form.

PATENT CLAIMS

1. Ink composition for ink-jetting upon substrates for a printing form comprising a substituted polymer or a copolymer, c h a r a c t e r i z e d in that at least one of said substitutions is an amide.

2. Ink according to claim 1, c h a r a c t e r i z e d in that said substitutions is a secondary amide.

3. Ink according to claim 1, c h a r a c t e r i z e d in that said substitutions is a primary amide.

4. Ink according to any of the preceding claims, c h a r a c t e r i z e d in that the polymer is a Joncryl polymer or equivalent to.

5. Ink according to any of the preceding claims, c h a r a c t e r i z e d in that the polymer is Joncryl 690 or equivalent to.

6. Ink according to any of the preceding claims, c h a r a c t e r i z e d in that the polymer has an average mole weight above 10 000 g/moles.

7. Ink according to any of the preceding claims, c h a r a c t e r i z e d in that the polymer has an average mole weight above 14 000 g/moles.

8. Ink according to any of the preceding claims, c h a r a c t e r i z e d in that it further comprises at least one of the following components:

a) from 0.1 to 20 % by weight of a surfactant,
b) from 0.1 to 20 % by weight of a colour,
c) from 0 001 % by weight to saturation of one or more fatty acids, oils or alcohols,
d) from 0.001 to 10 % by weight of at least one metal or metal complexes from the group of transition metals,
e) from 0.1 to 80 % by weight of a surface tension/viscosity modifying agent,
f) from 0.01 to 20 % by weight of another additive,
g) from 5 to 90 % by weight of water.

9. Ink according to claim 6, c h a r a c t e r i z e d in that the colour is soluble in the mixture.

10. Ink according to claim 3, c h a r a c t e r i z e d in that said fatty acid is lanoline or the lanolinate-alcohols

11. Ink according to claim 6, c h a r a c t e r i z e d in that the additive e) is chosen from the list: ethylene glycol monomethyl ether, ethylene glycol dimethyl ether, ethylene glycol monoethyl ether, ethylene glycol diethyl ether, ethylene glycol mono-n-propyl ether, ethylene glycol monoisopropyl ether, ethylene glycol mono-n-butyl ether, ethylene glycol mono-sec-butyl ether, ethylene glycol monoisobutyl ether, ethylene glycol mono-tert-butyl ether, ethylene glycol mono-n-amyl ether, ethylene glycol mono-n-hexyl ether, propylene glycol monomethyl ether, propylene glycol dimethyl ether, propylene glycol monoethyl ether, propylene glycol diethyl ether, propylene glycol mono-n-propyl ether, propylene glycol monoisopropyl ether, propylene glycol mono-n-butyl ether, propylene glycol mono-sec-butyl ether, propylene glycol monoisobutyl ether, propylene glycol mono-tert-butyl ether, diethylene glycol monomethyl ether, diethylene glycol dimethyl ether, diethylene glycol monoethyl ether, diethylene glycol diethyl ether, diethylene glycol mono-n-propyl ether, diethylene glycol mono-isopropyl ether, diethylene glycol mono-n-butyl ether, diethylene glycol mono-sec-butyl ether, diethylene glycol monoisobutyl ether, diethylene glycol mono-tert-butyl ether, dipropylene glycol monomethyl ether, dipropylene glycol monoethyl ether, dipropylene glycol mono-n-propyl ether, dipropylene glycol mono-n-butyl ether, polyethylene glycol monopropyl ether, polyethylene glycol monobutyl ether, ethylene glycol, propylene glycol, any alcohol with 1 to 6 carbon atoms e g methanol, ethanol, n-propanol, 2-propanol etc.

12. Ink according to claim 6, c h a r a c t e r i z e d in that said metal or metal complex is chromium, titanium, iron, molybdenum, manganese, cobalt, zirconium or vanadium.

13. Ink according to claim 6, c h a r a c t e r i z e d in that it comprises at least one liquid.

14. Ink according to claim 11, c h a r a c t e r i z e d in that at least one liquid is water.

15. Ink according to claim 1-12, c h a r a c t e r i z e d in that it has a surface tension between 0.02 and 0.06 N/m.

16. Ink according to any of the preceding claims, c h a r a c t e r i z e d in that it has a surface tension between 0.03 and 0.05 N/m.

17. Ink according to claim 1-12, c h a r a c t e r i z e d in that its pH is kept above 7.

18. Ink according to claim 1-12, c h a r a c t e r i z e d in that its pH is between 7.5 and 8.5.

19. Ink according to claim 1-12, c h a r a c t e r i z e d in that it has a viscosity between 1 5 and 4.5 mPa·s.

20. Process for producing ink, c h a r a c t e r i z e d in that it comprises the steps:

a) treating an acid containing polymer or a copolymer with an amine,
b) adjusting pH to above 7,
c) optionally adding fatty acid, oil or wax,
d) optionally adding one or more transition metals,
e) optionally adding colour.

21. Process according to claim 21, c h a r a c t e r i z e d in that the amine is ammonia

22. Process according to claim 21, c h a r a c t e r i z e d in that further base is added in order to keep pH between 7.5 and 8.5

23. Process according to claim 21, c h a r a c t e r i z e d in that the polymer or copolymer comprises at least one of the monomers: acrylic acid, methacrylic acid, maleic acid, maleic acid anhydride, fumaric acid, fumaric acid anhydride, styrene, sulfonated styrene, and vinyl.

24. Process according to claim 21, characterized in that the mixture is heated to between 65 °C and 140 °C

25. Process according to claim 21, characterized in that the mixture is heated to between 70 °C and 100 °C

26. Process according to claim 21, characterized in that the mixture is heated to about 80 °C

27 Process according to claim 21, characterized in that the fatty acid is chosen from the list: lauric, myristic, palmitic, stearic, arachidic, palmitoleic, oleic, linoleic, linolenic acids, lanoline and lanolinate-alcohols.

28. Process according to claim 21, characterized in that the fatty acid is lanolin or lanolin alcohols

29. Process according to claim 21, characterized in that the mixture is treated at a pressures different from 1 atm

30. Process according to claim 21, characterized in that the mixture is treated at a pressures from 0.1 atm to 150 atm

31. A method of preparing a lithographic print form, characterized in that it comprises the steps:

a) treating a substrate with an Ink according any of the claims 1 to 19,
b) drying the substrate,
c) heating the substrate.

32. A method according to claim 31, characterized in that the substrate is heated to above 150 °C.

33. A method according to claim 31, characterized in that the substrate is heated to between 170 °C and 220 °C.

34. A method according to claim 31, characterized in that the substrate is heated to between 190 °C and 210 °C.

35. A method according to claim 31, characterized in that the substrate is a metal plate.

36. A method according to claim 31, characterized in that the substrate is an aluminium plate.

37. A method according to claim 31, characterized in that the ink is burned into the substrate.